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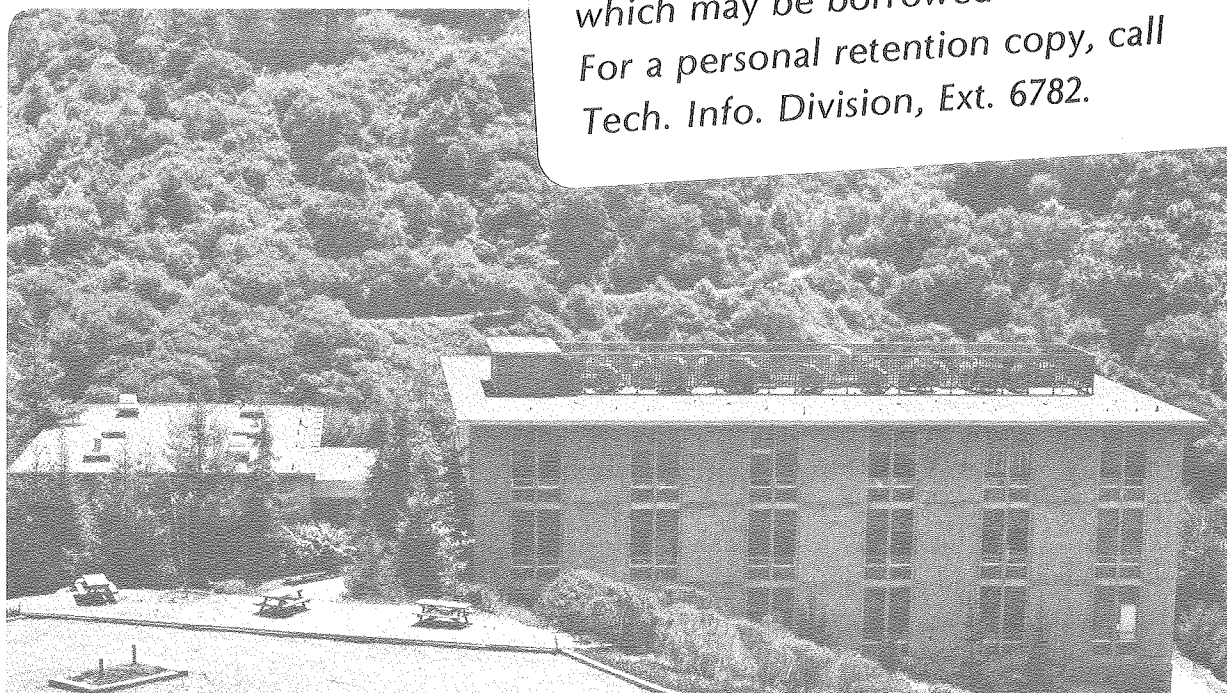# Orientation Relationships in Precipitation Systems

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ABSTRACT

Based on a survey of the literature on orientation relationships in precipitation systems   a unified view of all the known relationships in bcc/hcp and bcc/fcc systems is presented. Within each set of crystal systems, orientation relationships are closely connected by small fixed rotations whose magnitude depends only on crystal symmetries. Close parallels exist between the two sets of crystal systems, bcc/fcc and bcc/hcp. The regularities observed in the literature survey lead to the hypothesis that precipitate and matrix tend to be related by an invariant line strain. The relative rotation of the two lattices predicted by this hypothesis is determined as a function of the lattice parameter ratio and is consistent with a large number of experimental studies. In the analysis of simple non-coherent precipitate morphologies the criterion of directional mismatch is demonstrated to be superior to the commonly used planar mismatch criterion. The precipitate morphology sensitively reflects variations in orientation relationships. Morphologies of coherent and equilibrium semicoherent precipitates are governed by more complex criteria but are also dominated by basically crystallographic requirements.

INTRODUCTION

The orientation relationship (OR) between two phases of different crystal structure is important because it has a strong bearing on

microstructure-property relationships. Of the many processes in which OR's play a crucial role, the nucleation, growth and distribution of carbides or nitrides in steels, the formation of martensite, or the epitaxial growth of one phase on the surface of another are only a few examples. Many papers have been published analysing precipitate morphologies and interphase interfaces in terms of OR's which were found experimentally, mainly by selected area diffraction in transmission electron microscopy. Usually the OR of a precipitate is established as an experimental fact and the morphology is rationalized in terms of low index planes with minimum mismatch. This mode of analysis is the most common and follows naturally from the experimental determination of an OR by electron diffraction. Spots in the diffraction patterns are reflections with non-zero structure factor arising from sets of crystallographic planes. Only low-order reflections are normally recorded and analysed. A typical analysis searches for an orientation in which the matrix and the precipitate appear simultaneously in some low-index zone. When this is the case, the directions of the two zone axes are approximately parallel. If a matrix and a precipitate spot within this zone lie along the same direction, the corresponding crystallographic planes are parallel. Hence it is common practice to express OR's in terms of a plane and a direction in the precipitate which are parallel to a plane and a direction in the matrix. With this information, an OR can be plotted on a composite stereographic projection.

Using either the stereogram or the diffraction patterns directly, one can look for poles or reflections which are close together. While the stereogram displays only angular relationships between the crystallographic planes in three dimensions, a diffraction spot pattern shows both angles

and spacings between planes, but only in a two-dimensional section. Hence if a precipitate spot is close to a matrix spot, the corresponding crystal planes are nearly parallel and have a small mismatch. If is often concluded that precipitate growth will be easy, normal to such a plane. This method of morphological analysis has been used with remarkable success in a variety of systems. Typical examples are the work of Dyson et. al.[1] on {100} needles of Mo_2C in ferrite and Potter's[2] more complex case of twinned {112} plates of V_3N in vanadium.

The type of analysis described above is limited in three ways;
1) Only low-index poles or reflections are considered which often leads to an over-simplification of OR's. This is partly the reason for the relatively small number of OR's that are well established. Between fcc and bcc structures, the best known OR's are the ones determined by Bain[3], Nishiyama and Wassermann (NW)[4,5] and Kurdjumov and Sachs (KS)[6] while those of Greninger and Troiano (GT)[7] and Pitsch[8] are less widely known. Between bcc and hcp structures, only the Pitsch and Schrader (PS)[9] and the Burgers[10] OR are well-known and that of Potter[2] has been found only recently. The Jack OR[11] contains elements of both the Burgers and the Potter OR and is usually only approximate. As will become clear later, it is desirable to increase the accuracy of experimental determinations by the use of microdiffraction[12], Kikuchi lines[13], or high angle tilting[14].

2) As a result of the analysis of electron diffraction patterns in which spots represent crystal planes, only the matching of planes is usually considered. However, Murphy and Whiteman[15] in their analysis of epsilon carbide in martensite, as well as Bywater and Dyson[16] in their work on Cr_2N in steels recognized the importance of directional rather than

planar misfit. This point will be shown more clearly in the course
of this paper.

3) The most important limitation of a conventional analysis is that it
cannot predict an OR from first principles. One can explain particle
morphologies if the OR is known[2], or for a given morphology rationalize
why one OR is more favorable than another[17], one can even postulate an
OR if the morphology is known[18], but so far there has been no study which
has predicted both OR and morphology from first principles. An attempt to
find theoretical limits for OR's was made independently by Sleeswyk[19]
and Ryder and Pitsch[20]. On the assumption that one plane and one
direction within that plane remain unrotated, Sleeswyk[19] derived a "scatter
region" for the OR between austenite and cementite while Ryder and Pitsch[20]
used the same hypothesis to find an "orientation region" for grain boundary
precipitatesof Fe in a CoFe alloy. The "zero misfit analysis" of Lupton
and Warrington[21] made use of Sleeswyk's hypothesis to predict OR's between
ferrite and cementite in pearlite nucleated in a eutectoid steel. The
"scatter region" derived from Sleeswyk"s hypothesis is in excellent
agreement with experiments but does not allow the prediction of OR's
accurate enough to distinguish between any of the OR's mentioned above.

A completely different approach is that of Jack[22,23] who analysed
OR's of interstitial phases in terms of different coordinations of
interstitial atoms. His approach is the most lucid one because of its
physical meaning but it is limited to interstitial phases and can only
make rough predictions. Along similar lines, Andrews et. al.[24] developed
an understanding of the similarities and differences of precipitate and
matrix structures for cementite[25], epsilon carbide[26] as well as M_7C_3
carbide[27] precipitates in a ferrite matrix. While giving a good

explanation of the individual atomic rearrangements involved, these models do not permit a prediction of OR's.

It is clear from this brief review that in spite of different attempts no unique method has been found capable of predicting OR's and morphologies accurately. In the present paper it is shown how the concept of the invariant line can be used to unify the different approaches to OR prediction, and to illuminate the fundamental mechanisms involved. A comparison of the available experimental evidence on OR's with the predictions shows excellent agreement. Since by far the greatest number of all experimentally determined OR's concern the precipitation in bcc/fcc or bcc/hcp systems, the theory is developed using the example of these two groups of systems. It will therefore be useful to review the known OR's for each group, their interrelationships within each group, and the connections between the two groups.

A Systematic View of the known Orientation Relationships

A well-known commonality of OR's is that close-packed planes in the two structures tend to be parallel. The atomic arrangement of two superimposed close-packed planes is shown in Fig. 1(a). Open circles represent the atoms in a {110} bcc plane, solid circles show the hexagonal arrangement of the atoms in either a {111} fcc or an (0001)hcp plane. The symmetries of these two-dimensional arrangements are twofold and sixfold rotations as emphasized by the rectangle connecting the atoms in the bcc close-packed plane and the hexagon connecting the atoms in the fcc (or hcp) close-packed plane. In spite of their different symmetries the two atomic arrangements are obviously very similar. As is well-known, two small orthogonal strains are sufficient to produce one lattice from the other.

In the position of highest composite symmetry shown in Fig. 1(a) these two strains lie along the <001> and <1$\bar{1}$0>bcc directions. One consequence of this choice of strain is that the close-packed directions in the two lattices are misaligned by an angle of 5.26°. It should be emphasized that this angle is independent of the relative lattice parameters of the two structures and is entirely determined by their respective symmetries. A rotation of one of the lattices through this angle of 5.26° will bring one set of close-packed directions into coincidence. This new configuration is shown in Fig. 1(b). The overall symmetry of this rotated arrangement is obviously lower than in Fig. 1(a); the rotation has destroyed the two mirror planes normal to the principal axes of the strain.

Specialized as they may seem, these two arrangements of atoms in close-packed planes describe the four largest groups of OR's reported in the literature, those of Nishiyama-Wassermann (NW) and Kurdjumov-Sachs (KS) in bcc/fcc systems and those of Pitsch-Schrader (PS) and Burgers in bcc/hcp systems. These four OR's are illustrated in stereographic projections in Figs. 2 and 3. All four stereograms are projected normal to the close-packed planes in the two structures in order to match with Fig. 1. Open circles represent bcc poles, solid circles fcc or hcp poles. The indices of fcc poles are underlined and those of hcp poles are given in four-index notation. As a reminder of the atomic arrangements in the close-packed planes, a rectangle and a hexagon have been outlined in the stereograms in their relative positions. The more symmetric unrotated OR's are shown in Figs. 2(a) and 3(a). In the bcc/fcc case, this is known as the Nishiyama-Wassermann (NW) OR and in the bcc/hcp case the Pitsch-Schrader (PS) OR. A relative rotation of 5.26° brings NW to the

Kurdjumov-Sachs (KS) OR and PS to the Burgers OR (Figs. 2(b) and 3(b)).

The analogy between the two sets of crystal systems can be carried further. Just as the 5.26° rotation brought two new low-index poles into coincidence, so can a second rotation around these newly coincident poles bring another set of low-index planes into coincidence. This new axis of rotation is shown in Figs. 2(b) and 3(b) and the poles brought into coincidence are (001)fcc with (101)bcc in Fig. 2(b) and ($\bar{1}$011)hcp with (101)bcc in Fig. 3(b). In the bcc/fcc case this produces the Pitsch OR while in bcc/hcp it results in the OR first reported by Potter. All of these rotations are independent of the lattice parameters of the two phases (except the Burgers-to-Potter rotation which depends on the c/a-ratio of the hcp phase).

In principle any OR can be related to a standard OR such as NW or PS by a given rotation. While the three sets of analogous OR's illustrated above cover all the well-known OR's for bcc/hcp systems, there are two more in bcc/fcc systems which have no counterpart in bcc/hcp. One of these is the Greninger and Troiano (GT) OR intermediate between NW and KS. The rotation angle is 2.5° from NW. The other one is the famous Bain OR which can be produced from NW by a 9.74° rotation around [001]bcc to bring into coincidence (010)fcc with (010)bcc and (001)fcc with (101)bcc as well as (100)fcc with (10$\bar{1}$)bcc. This is clearly evident from Fig. 2(a) which also shows that axis of rotation. Because of its importance, the Bain OR is shown separately in Fig. 4. The fourfold rotational symmetries of the two crystal structures are symbolized by square outlines. Again solid circles are fcc poles with the corresponding indices underlined. The axis of rotation which produces the NW OR of

Fig. 2(a) is shown. Because of the four-fold composite symmetry of the Bain OR, there are four such rotation axes, each one producing a different variant of the NW relationship. In addition there is another set of four equivalent rotation axes, at 45° to the ones mentioned above. A 9.74° rotation around any of these axes produces the "inverse NW"[28] OR which is identical to the Pitsch OR. The rotation axis relating the Bain OR to the particular variant of the Pitsch OR mentioned in Fig.2(b) is also indicated in Fig. 4. From these two figures it is clear that the Pitsch OR is connected to both the KS and the Bain OR, and the interrelations are shown in a diagram in Fig. 5. This diagram does not exist for the bcc/hcp case because there is no counterpart to the high-symmetry Bain OR.

In summary, the unified description of the major OR's which has been given above has two important merits;

1) It demonstrates that all the well-known OR's of one set of crystal systems are connected with each other by some small relative rotation and are therefore not as radically different as they might seem.

2) A comparison of two different sets of crystal systems (bcc/fcc and bcc/hcp) shows them to be largely analogous.

The Invariant Line

A familiar concept in the crystallographic theories of phase transformations is that of a lattice correspondence and a transformation strain[29]. The Bain correspondence and the Bain strain[3] give an example so well-known it need not be illustrated here. The lattice correspondence describes a unit cell in the parent lattice which can be deformed by the transformation strain to become a unit cell in the product lattice. The

transformation strain is a homogeneous deformation applied equally to all unit cells in a crystal. Originally meant only for a discrete point lattice, i.e. the atoms on the corners of the unit cell, the transformation strain is identical to a strain describing a continuum deformation. This interplay between continuum and crystallography is essential to a number of important concepts as for example the theory of martensitic transformations[31,32,33] and 0-lattice theory[34]. A homogeneous strain, whether describing the rearrangement of discrete lattice points or the deformation of a continuum, can be expressed mathematically as a linear homogeneous transformation given by a transformation matrix $\hat{A}$. It can be shown that for such a transformation, lines remain lines and planes remain planes, but angles and lengths may be distorted[29].

The transformation strain, as it applies to bcc/hcp transformations, is illustrated for two dimensions in Figs. 1(a) and 6(a), representing the superposition of a bcc and an hcp close packed plane. A unit cell in the bcc lattice - for example all the open circles in Fig. 1(a) - is transformed into a unit cell in the hcp lattice (solid circles) by an expansion b along the y-direction and a contraction a along the x-direction. This defines both the lattice correspondence and the transformation strain. The two axes x and y are the principal axes of the transformation and the operation may be written as the diagonal matrix $\hat{A} = \begin{pmatrix} a & 0 \\ o & b \end{pmatrix}$ when related to the principal coordinate system. The length of a vector u will change to $|v| = |\hat{A} u|$ during the transformation. This is the well-known description of the deformation of a circle ($u_x^2 + u_y^2 = 1$) into an ellipse ($v_x^2/a^2 + v_y^2/b^2 = 1$) with major axes a and b. An illustration of this continuum deformation is given in Fig. 6(a) where the circle

represents the bcc and the ellipse the hcp close-packed plane. Any radius vector on the circle will in general change both length and direction during the transformation. A special vector is the one ending at point B because it changes direction from B to B' but its length is preserved. If the directional change from B to B' is compensated by a rigid body rotation of the transformed structure (ellipse) it will become an invariant line, a direction in the crystal which remains unrotated and unstretched during the transformation. This is shown for a continuum transformation in Fig. 6(b) and for discrete lattices in Fig. 1(b). Fig. 1(b) shows that the invariant line may be visualized as a row of atoms which is common to both structures. Due to the special choice of lattice parameters in Fig. 1(b), the invariant line coincides with a low-index (close-packed) crystallographic direction. This will not usually be the case and the invariant line can be any non-rational direction. It can be shown quite generally that any transformation strain relating two lattices may be changed to a plane strain by a rigid body rotation if one of the three principal strains is opposite to the other two[34]. The most general plane strain is identical to an invariant line strain. (Note that an invariant plane strain as used in the theory of martensitic transformations is a special case of an invariant line strain).

As a basis for the prediction of OR's, it is now hypothesized that a precipitate lattice tends to be related to the matrix lattice by an invariant line strain. The invariant line lies in the precipitate/matrix interface. A habit plane which contains an invariant line and another direction of small strain can minimize the elastic strain energy of a coherent plate shaped nucleus. After the loss of coherency, the inter-face and hence the morphology of the semicoherent precipitate, is

determined by the minimum interfacial energy such as defined by Bollmann and Nissen[35]. In general, this semicoherent interface will be different from the coherent habit plane sharing with it only the invariant line[36].

For the present purpose, the hypothesis that an invariant line strain is produced by a small rotation around one of the principal axes of the transformation strain is sufficient to analyze and predict OR's. The angle of this rotation, such as shown in Figs. 1 and 6, can be determined by matrix algebra. Any linear homogeneous transformation $\hat{A}$ may be decomposed into a rigid body rotation $\hat{R}$ through some angle θ and a pure deformation $\hat{D}$[37]. If the matrix $\hat{D}$ is referred to the principal axes of the deformation it has only diagonal elements. Thus, in two dimensions,

$$\hat{A} = \hat{R}\,\hat{D} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} a & 0 \\ o & b \end{pmatrix} \ .$$

A vector $\underset{\sim}{u}$ is an invariant line if it is unchanged under the operation $\hat{A}$:

$$\hat{A}\,\underset{\sim}{u} = \underset{\sim}{u} \quad \text{or} \quad (\hat{A}-\hat{I})\,\underset{\sim}{u} = 0$$

and $\det |\hat{A}-\hat{I}| = 0$,

i.e.
$$\det \begin{vmatrix} a\cos\theta - 1 & b\sin\theta \\ -a\sin\theta & b\cos\theta - 1 \end{vmatrix} = 0$$

which when solved for θ gives

$$\cos\theta = \frac{1+ab}{a+b} \tag{1}$$

Recognizing that the principal distortions a and b must have a constant ratio for a given bcc/fcc or a bcc/hcp transformation, the angle θ simply becomes a function of the dimensionless parameter $\dfrac{a_{hcp}}{a_{bcc}}$ (or $\dfrac{a_{fcc}}{a_{bcc}}$). This plot applies to the rotation of two close-packed planes as they are shown

in Fig. 1. Note that θ varies rapidly between zero and a flat maximum at 5.8$^{\mathrm{o}}$. The dotted line in Fig. 7 indicates $\theta = 5.26^{\mathrm{o}}$, the rotation that makes close-packed directions parallel, as in Fig. 1(b), whereas no rotation ($\theta=0^{\mathrm{o}}$) is shown in Fig. 1(a). Figs. 2 and 3 show in stereograms the OR's corresponding to the no-rotation line (PS and NW) and the 5.26$^{\mathrm{o}}$ rotation line (Burgers and KS). Assuming an experimental error limit of $\pm 0.5^{\mathrm{o}}$, all systems lying on the curve in Fig. 7 having lattice parameter ratios between 1.21 and 1.36 would be experimentally determined as belonging to the Burgers OR (KS OR in bcc/fcc). According to Ryder and Pitsch, the error limit for OR's determined by conventional electron diffraction is even larger[38]. Hence most of the experimental evidence does not permit a distinction between for example an exact Burgers OR and one that lies within $\pm 0.5^{\mathrm{o}}$ of Burgers. In other words, the experimental data fits equally well the prevalent crystallographic idea which allows only zero and 5.26$^{\mathrm{o}}$ rotation and the continuum concept proposed here which allows a continuous spectrum of rotation.

Comparison of predicted and observed orientation relationships

In Fig. 7, the experimental data of 12 different bcc/hcp systems are shown in relation to the curve predicted by an invariant line rotation. Only three different OR's have been reported; the PS-OR ($\theta=0^{\mathrm{o}}$), the Burgers OR ($\theta=5.26^{\mathrm{o}}$), and the Potter OR (denoted by open circles, $\theta=5.26^{\mathrm{o}}$ plus another small rotation ϕ around the close-packed directions). The experimental OR's for ten out of 12 systems lie within $\pm 0.5^{\mathrm{o}}$ of the predicted value. The Burgers OR was found in seven systems, mostly transition metal carbides and nitrides, namely Mo_2C in Mo[39], Nb_2C in Nb[40], V_2C in V[41], W_2C in W[42], epsilon carbide in Fe[43,44], Cr_2N in Fe[16] and the

ζ-phase in β-Al-Ag[45]. As evident from Fig. 7, only Cr_2N in Fe is more than 0.5° from the predicted OR. The original reference[16] does not allow a closer examination of this discrepancy since the OR was determined in {100} sections instead of the necessary {110}.

The most striking effect was found in Mo_2C. When precipitating in ferrite is showed no rotation[1] while the same Mo_2C in a molybdenum matrix followed the Burgers OR[39]. This significant difference has not been explained before but now becomes clear from the viewpoint of the present approach; the lattice parameter ratio for Mo_2C in ferrite clearly lies outside the range for which rotations are predicted (see Fig. 7).

The case of bcc/fcc systems is complicated by the existence of a larger number of low-index OR's due to the higher overall symmetry. However, the same principle can be applied and tested on a number of systems. A test case analogous to Mo_2C in a ferrite or a molybdenum matrix is bcc iron, vapor deposited on {111} surfaces of different fcc materials. When deposited on silver or gold substrates, the lattice parameter ratio a_{fcc}/a_{bcc} is larger than $\sqrt{2}$, no rotation is predicted, just as for Mo_2C in ferrite. Experimental evidence confirmed that the NW OR was followed strictly[46]. On other fcc substrates such as copper or nickel a_{fcc}/a_{bcc} is smaller than $\sqrt{2}$ and a rotation ranging from 0 to 5.26° has been reported[47,48] where the theory predicts 5.4 and 5.7°. Echigoya et. al.[48] attempted to explain this result by optimizing an "area of good fit", first introduced by Hall et. al.[49]. It can be shown analytically however, that any such area of good fit must be independent of rotation. Variations occur only as an artifact when using graphical instead of analytical techniques. On the otherhand, the predictions of

the present theory are in good general agreement with these experiments.

A spread of OR's such as observed for Fe on Ni and Cu substrates has also been found in other systems, for example Cr in Cu-Cr alloys[28,49]. Such variations would be expected whenever the interfacial energy, or the coherency strain energy has only a shallow minimum at the OR which provides an invariant line.

Returning to cases for which the observed spread of OR's is negligible, such as the refractory bcc/hcp systems it can be shown that even the subtle difference between the Burgers and the Potter OR is predictable in the present approach. Fig. 3(b) illustrates that these two OR's are related by a small rotation around a common close-packed direction. The exact amount of rotation depends on the c/a - ratio of the hexagonal system, but is usually less than 2°. As before, we can compare this crystallographically determined angle to the angle of rotation necessary for an invariant line, take into account experimental error limits, and compare the predicted OR's with the ones observed. The principal distortions a and b are now related to a new set of crystallographic axes, the coincident poles of Fig. 3(b). With the axis of rotation along the close-packed direction, a plot of the rotation angle ϕ versus lattice parameter ratio a_{hcp}/a_{bcc} looks similar to Fig. 7. This is shown in Fig. 8 for some slightly different c/a - ratios. On the line of no rotation (abscissa), the OR is that of Burgers, and the Potter OR is indicated by horizontal lines at angles ϕ which depend on the c/a - ratio. Note that a rotation is possible ($\phi \neq 0$) only when the lattice parameter ratio is between 1.23 and 1.33, the crossover points of the curve in Fig. 7 with the $\theta = 5.26^{o}$ (Burgers) line. This simply means that within this bracket of rotation,

the Burgers OR is reached before an invariant line is produced. An invariant line can therefore be found by either a continued rotation around the same axis — beyond 5.26° — or by using a newly established rotation axis (the close-packed direction) perpendicular to the first axis (the normal to the close-packed planes). The second possibility usually leads to the smallest total rotation and is observed experimentally. This is shown in Fig. 8 for the systems Nb_2N in Nb, Ta_2N in Ta, V_3N in V and Ta_2C in Ta, all of which fall into the critical range of lattice parameter ratios a_{hcp}/a_{bcc} (open circles in Fig. 7). All these systems were experimentally determined to follow the Potter OR and deviate less than 0.5° from the OR's predicted on the basis an invariant line. Hence the same principle which explains the different OR's of Mo_2C when precipitated in ferrite or in molybdenum can be used to show why and how far some systems deviate from the parallelism of close-packed planes.

The AgAl system investigated by Plichta and Aaronson[45] also falls into this range and should, but does not, exhibit the Potter OR, manifested in a 1° misorientation between the close packed planes. Since these investigators used an accurate method for the determination of OR's, this misorientation is beyond experimental error limits. The reason for this system to have close packed planes in both matrix and precipitate exactly parallel must be the fact that the precipitates are grain boundary nucleated. The OR could thus be determined by the interface energy criterion as given by Bollmann and Nissen[35]. This criterion was in fact applied successfully to this system by Plichta and Aaronson[45], and subsequently, their computer results were shown to predict an invariant line[36].

Morphology – planar versus directional matching

As mentioned earlier, precipitate morphologies have often been rationalized in terms of their corresponding OR's. The criterion commonly used is that of minimum planar mismatch. It is now shown that this criterion, based on an analysis of electron diffraction patterns, is in error. Fig. 9 illustrates a typical situation in the study of OR's using the familiar example of two close-packed planes, one in a bcc lattice (open circles) and one in an hcp lattice (full circles). The corresponding electron diffraction pattern has been drawn in Fig. 9(b). From this spot pattern, the OR would be analyzed as $[0001] \parallel [110]$ and $(10\bar{1}0) \parallel (\bar{1}1\bar{2})$, obviously the Burgers OR. (Note that in this particular case directions and planes are interchangeable). The most common mode of analysis will then identify spots in the diffraction pattern which are close together, such as $(20\bar{2}0)$ and $(\bar{1}1\bar{2})$. These two sets of planes are parallel and have a small mismatch in spacing. Hence precipitate growth should be easy, normal to these planes, in a $[\bar{1}1\bar{2}]$ direction. That this is a misconception can be seen by going back to the real space configuration. Atoms in the $(\bar{1}1\bar{2}) \mid (10\bar{1}0)$ planes, indicated by lines, are related by a shear. This shear has no effect on the plane spacing but it will obviously lead to large distortions if a precipitate grows normal to these planes. There is, however, a direction in which the distortions are small. In Fig. 9(a) this is the close-packed direction $[\bar{1}11]$. Thus the criterion of directional matching predicts an easy-growth direction at right angles to the one predicted on the basis of planar matching.

The example in Fig. 9 was chosen because of its simplicity. However, the principle can be expressed more generally using matrix algebra. In

particular, the properties of reciprocal space are known to be reciprocal to those of real space. If the real space lattices of matrix and precipitate are related by a matrix $\hat{A}$ their reciprocal lattices are related by $\left(\hat{A}^{-1}\right)^T$, the transpose of the inverse of $\hat{A}$[50]. The basis made by the three eigenvectors of $\hat{A}$ is reciprocal to that formed by the three eigenvectors of $\left(A^{-1}\right)^T$. The corresponding eigenvalues are the inverse of each other. Thus any direction of smallest mismatch in reciprocal space has a direction of smallest inverse mismatch in real space normal to it. Hence, even though the well-known direction-plane relationship between real and reciprocal space means that good directional match in reciprocal space implies a good <u>plane</u> matching in real space, it is the other implication which underlies the morphology; namely that good directional match in reciprocal space also means good <u>directional</u> match in real space, normal to the corresponding reciprocal space directions. As a special case, an invariant line in reciprocal space implies a perpendicular invariant line (not an invariant plane) in real space. The conclusion drawn from Fig. 9 is therefore valid in general.

Comparison of predicted and observed morphologies

Bywater and Dyson[16] have shown that all the experimental data available to them agreed with the criterion of directional mismatch. Implicity, their analysis rested on the assumption that precipitate growth will proceed best in the directions of small mismatch. The same argument will be used here by postulating that precipitate dimensions tend to be inverse to the directional mismatch. Before comparing the morphologies thus predicted with experimental observations, it should be emphasized that this is a rather simplifying assumption applicable only to non-coherent precipitates. Several important features involved in the determination of morphologies have been neglected, among them the structure and energy of the interface,

lattice anisotropies, and the mechanisms of coherency loss and of growth. In spite of these limitations, the assumption is a reasonable first approximation, particularly for the case of precipitates growing in a highly dislocated matrix where the loss of coherency and the structure of the interface are less important.

The OR's calculated in the preceding section would predict precipitate needles along the invariant line directions. The bcc crystallographic indices of the invariant line have been indicated below the curve in Fig. 7. A comparison with published experimental results shows good agreement. Mo_2C in Fe (lattice parameter ratio 1.49) forms <100> needles[1,51]. Cr_2N in Fe (ratio 1.37) forms <311> needles[16], ε-carbide in Fe (ratio 1.35) was reported as <211> needles[15]. The needle axis lie indeed in the regions predicted by the invariant line criterion. However all the systems within the range of rotations exceeding the 5.26^{o} necessary to reach the Burgers OR, show a platelike morphology. The most striking feature, first reported by Potter[2], is extensive twinning of the precipitate plates. This can be explained by the amount of rotation around the close packed direction which is required to produce an invariant line (see Figs. 3(b) and 8). For Ta_2N in Ta[52], Nb_2N in Nb[52] and V_3N in V[2], this rotation is within 0.1^{o} of the ideal Potter OR (See Fig. 8). If this ideal OR was followed exactly, pairs of two precipitate variants would be in twin orientation and could form a twinned precipitate in which both parts follow the same OR[53]. This can be seen most clearly by a hypothetical twinning operation on the (101) mirror planes of the matrix when matrix and precipitate are in the Potter OR.

As a symmetry operation of the bcc lattice it creates no boundary in the matrix while the same operation produces a ($\bar{1}$011) twin in the precipitate.

Hence the OR presents no barriers to twinning in those systems that follow the exact Potter OR. It is well-known that twinning can relieve long-range stresses in one direction and allow a change of morphology from needles to twinned plates. The origin of the twins, mechanical or growth-type, is formally of no importance though in practice they will of course be growth twins. It is worth noting that of the four systems falling in the range of the Potter OR three show twinning in almost every precipitate, however, Ta_2C in $Ta^{14,54}$ is rarely twinned. In this system, the invariant line rotation is almost one degree from the Potter OR. In twinned Ta_2C precipitates therefore, at least one of the twin-related parts must deviate from its ideal OR, or if they both follow the same OR, they are not in exact twin orientation. This could explain why twinned precipitates are rare in this one system and frequent in the other three.

In summary, most of the reported precipitate morphologies agree with the hypothesis of particle dimensions tending to be inverse to the directional mismatch. The direction of the precipitate needles follows the same trend as the invariant line, namely from <100> towards <111> with decreasing lattice parameter ratio. This direction is somewhat more sensitive to the ratio of lattice parameters than the OR. When the OR rotates through 5.26^O, the invariant line turns through $\sim 30^O$. A more striking indication of the delicate balance that determines particle morphologies is the transition from needles to twinned plates in the range of lattice parameter ratios between 1.23 and 1.33. The good agreement between the observed morphologies and the theory lends strong support to the invariant line hypothesis.

Other morphologies are expected and have been observed for large semicoherent precipitates with a well-developed interfacial structure and for fully-coherent small precipitates. In particular, it was found that small coherent plate-shaped precipitates follow a systematic pattern which is entirely consistent with the concept of an invariant line strain as the stress-free transformation strain. In contrast to current beliefs, it was concluded that the OR and habit plane of plate-shaped coherent precipitates are dominated by crystallography rather than elastic anisotropy[55]. This conclusion is supported by the observation that, regardless of the elastic constants of the bcc matrix, coherent precipitate plates of both fcc and hcp structure were found on {100} planes when the lattice parameter ratio was to the right of the curve in Fig. 7,[18,56,57] and on or near {310} planes for a ratio of between 1.33 and 1.37[18,40,41,55]. The fact that this behavior was identical for fcc and hcp precipitates stresses once more the close similarities apparent from the OR's in Figs. 2 and 3.

When the precipitates loose coherency and form well developed semi-coherent interfaces with the matrix, the morphology can be predicted on the basis of a known OR by 0-lattice theory[33] or similar crystallographic arguments based on optimum matching at the interface[49]. Hence at any stage of a precipitation sequence, it should be possible to predict the corresponding morphology simply on the basis of the known equilibrium precipitate structure.

SUMMARY

In an attempt to understand and predict orientation relationships (OR's), a systematic review of the known OR's found in bcc/fcc and bcc/

hcp systems has shown strong similarities between the OR's in the two groups. All the different OR's within each group were found to be closely related by small relative rotations whose magnitude is determined by lattice symmetries alone and is independent of lattice parameters. Based on a survey of a large body of experimental data, however, it was determined that OR's depend critically on the relative lattice parameters of the phases involved, and it was hypothesized that two phases tend to be related by a general plane strain, i.e. an invariant line strain. The rigid body rotation around a principal axis that is necessary to convert a general transformation strain into an invariant line strain was calculated as a function of the lattice parameter ratio. It was found that the observed OR's in most precipitation systems clustered, within the range of experimental error, around the calculated OR's. A critical test was the 5° difference in OR which was found in both bcc/hcp and bcc/fcc systems when the lattice parameters ratio crossed a limiting value. The theory agreed well with these observations.

It was further shown that the criterion of planar matching often applied in the analysis of precipitate morphologies is in error and a better criterion is that of directional matching. Good agreement with experimentally determined morphologies indicated that this simple criterion was appropriate for the analysis of some non-coherent needle-shaped precipitates. The needle axis was predicted and confirmed to be much more sensitive to the lattice parameters ratio than the OR. Different criteria hold for plateshaped coherent or fully grown semicoherent precipitates, but in these two cases also, crystallography was found to be the dominating factor.

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FIGURE CAPTIONS

Fig. 1.   Superposition of close-packed planes of bcc crystal (open

circles) and fcc or hcp crystal (full circles). The lattices

of open and full circles are related by small strains along x

and y directions in a). In b) a small relative rotation of

5.26° has brought close-packed directions into coincidence.

Fig. 2.   Composite stereograms showing the most common orientation

relationships in bcc/fcc systems, that of Nishiyama-Wassermann

in a) and Kurdjumov-Sachs in b). As in Fig. 1, open circles

represent bcc, full circles fcc poles. The two OR's are related by

a 5.26° rotation which is emphasized by the relative positions

of a rectangle and a hexagon symbolizing the symmetries of

close-packed planes in bcc and fcc lattices. The connection

with the orientation relationships of Bain and Pitsch are

indicated by their axes of rotation.

Fig. 3.   Composite stereograms showing the most common orientation

relationships in bcc/hcp systems, that of Pitsch-Schrader in

a) and that of Burgers in b). Open circles represent bcc,

full circles hcp poles. Note the complete analogy to bcc/fcc

systems shown in Fig. 2. The connection with the Potter

orientation relationship is indicated by its rotation axis -

note the parallel to Fig. 2(b).

Fig. 4.   The Bain orientation relationship as it would be produced by

rotation around the axis marked in Fig. 2(a). Open circles

are bcc, full circles fcc poles. Note the high composite

symmetry emphasized by the squares. Rotations of 9.74°

around the axes indicated lead to either the Nishiyama-
Wassermann or the Pitsch (also called inverse Nishiyama-
Wasserman) orientation relationship, cf. Fig. 2.

Fig. 5. Symmetry diagram pointing out the interrelationships between
different variants of the four main orientation relationships
in bcc/fcc systems. P=Pitsch, KS=Kurdjumov-Sachs, NW=Nishiyama-
Wassermann. The lines indicate small relative rotations.

Fig. 6. The lattice strain of Fig. 1 in continuum representation. The
circle (bcc plane) is transformed into an ellipse (fcc or hcp
plane) by a small strain. A small rotation bringing B and B'
into coincidence produces an invariant line, (b).

Fig. 7. Rotation angle θ necessary to produce an invariant line by
rotation around the normal to the close-packed planes, (see
Fig. 1), as a function of lattice parameter ratios (calculated
from equ. (1)). A 0° rotation leads to the Nishiyama-Wassermann
or Pitsch-Schrader relationships and a line at 5.26° rotation
marks the Kurdjumov-Sachs or Burgers relationships. The curve
indicates a continuous dependence on lattice parameter ratios.
Experimentally observed orientation relationships for twelve
different bcc/hcp systems are given by circles. Open circles
indicate a slight deviation from the parallelism of close-
packed planes, i.e. the Potter relationship.

Fig. 8. Plot of invariant line rotation ϕ as in Fig. 7, for bcc/hcp
systems in the range of the Potter relationship (open circles
in Fig. 7). Here the axis of rotation is the common close-
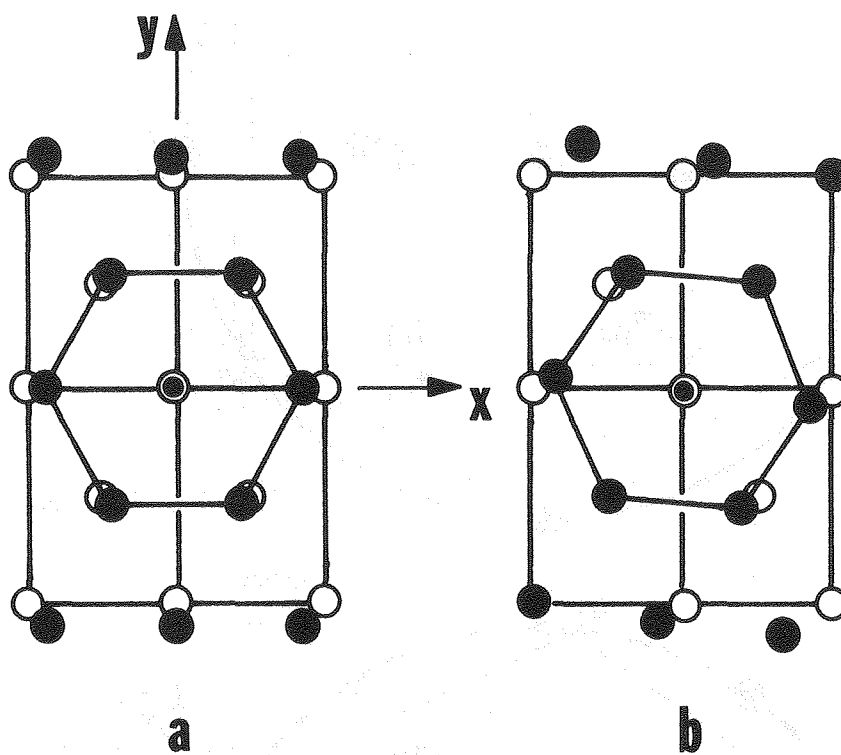packed direction. Curves are given for three different
c/a ratios.

Fig. 9. Real space lattice in Kurdjumov-Sachs or Pitsch-Schrader orientation relationship (a) and corresponding composite electron diffraction pattern (b). Good match in the $\langle\bar{1}1\bar{2}\rangle$ direction in the diffraction pattern implies an easy growth direction of $\langle\bar{1}11\rangle$, not $\langle\bar{1}1\bar{2}\rangle$.

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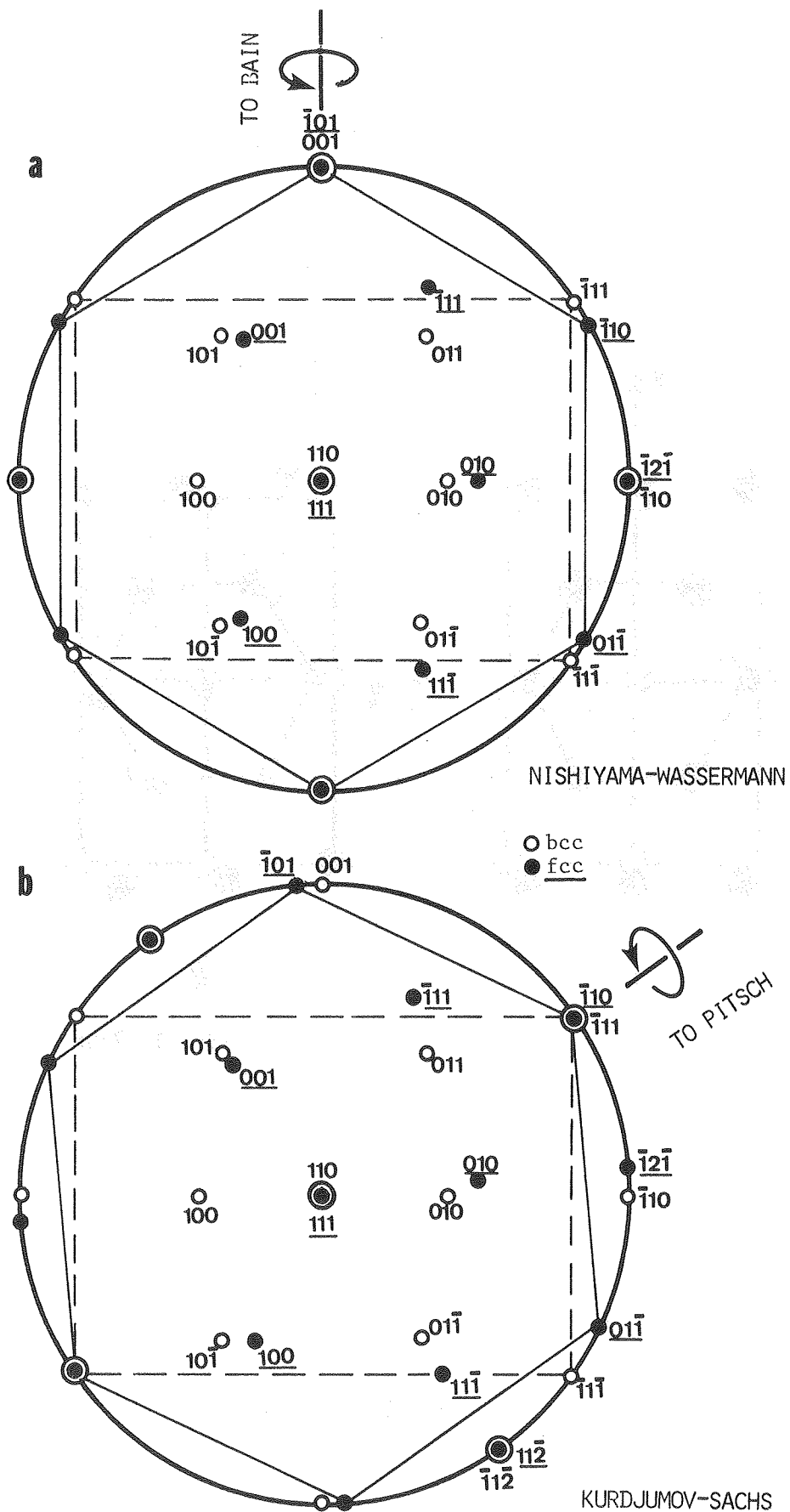
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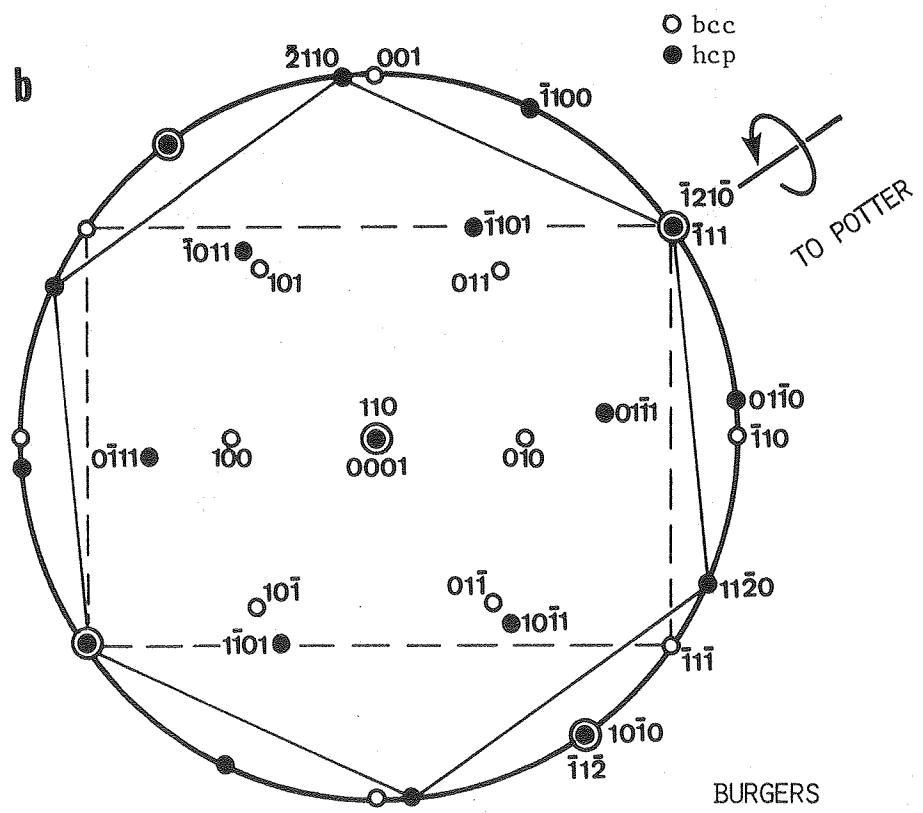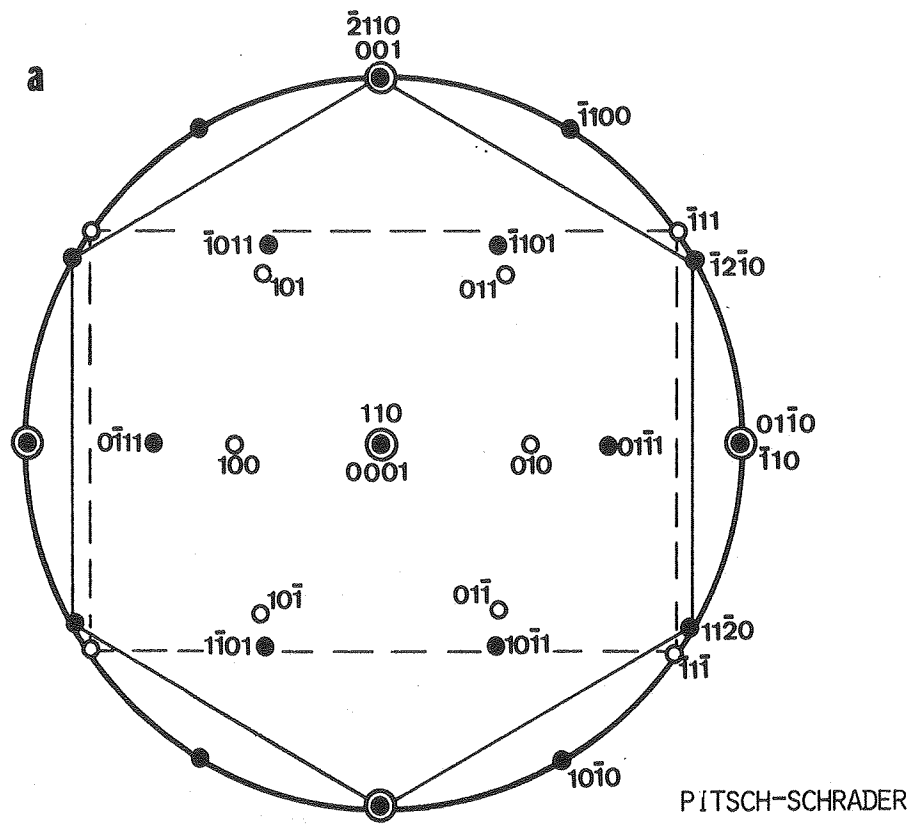a   b
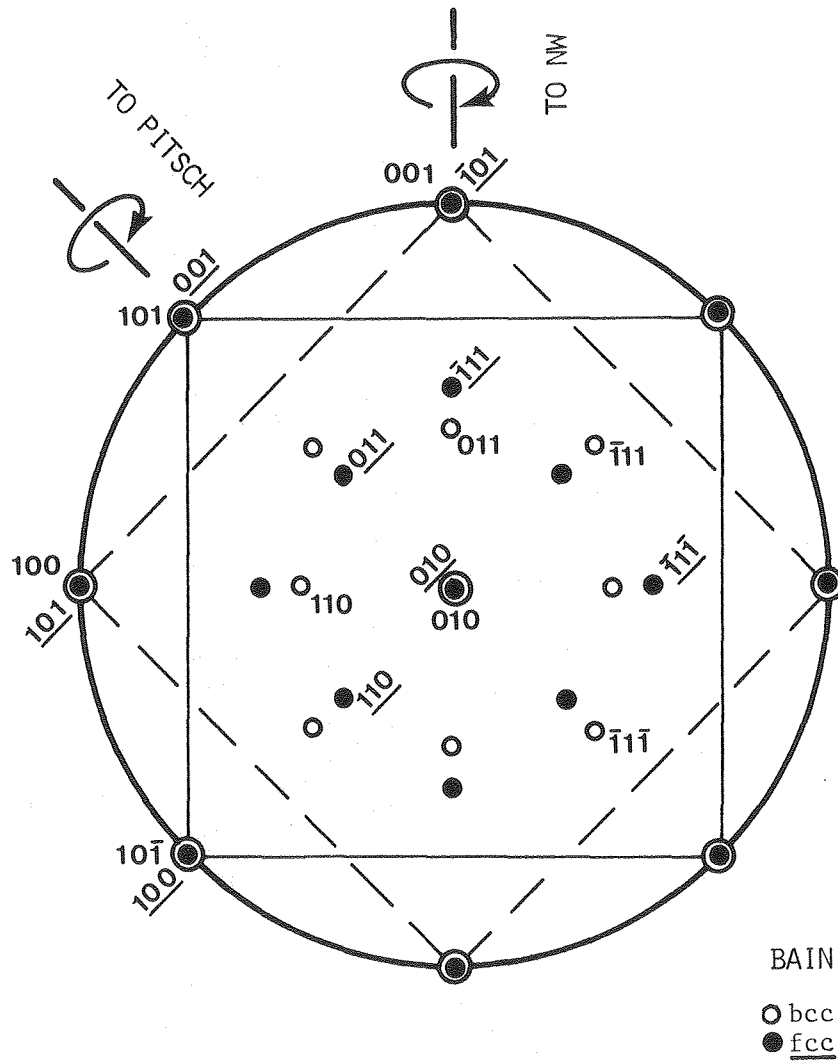
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Fig. 1

Fig. 2

NISHIYAMA-WASSERMANN

KURDJUMOV-SACHS

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Fig. 3

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Fig. 4

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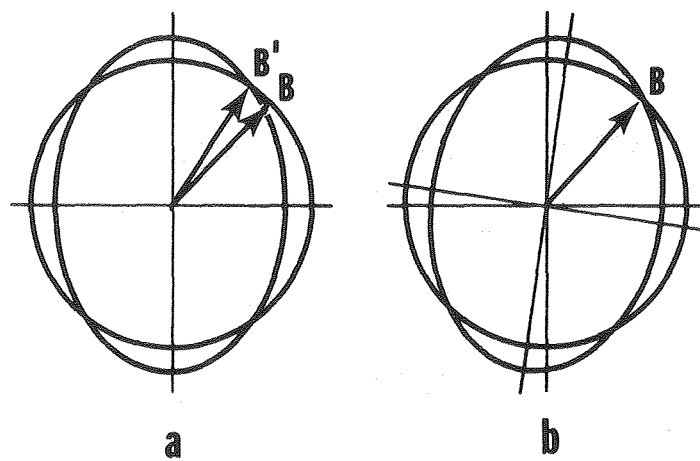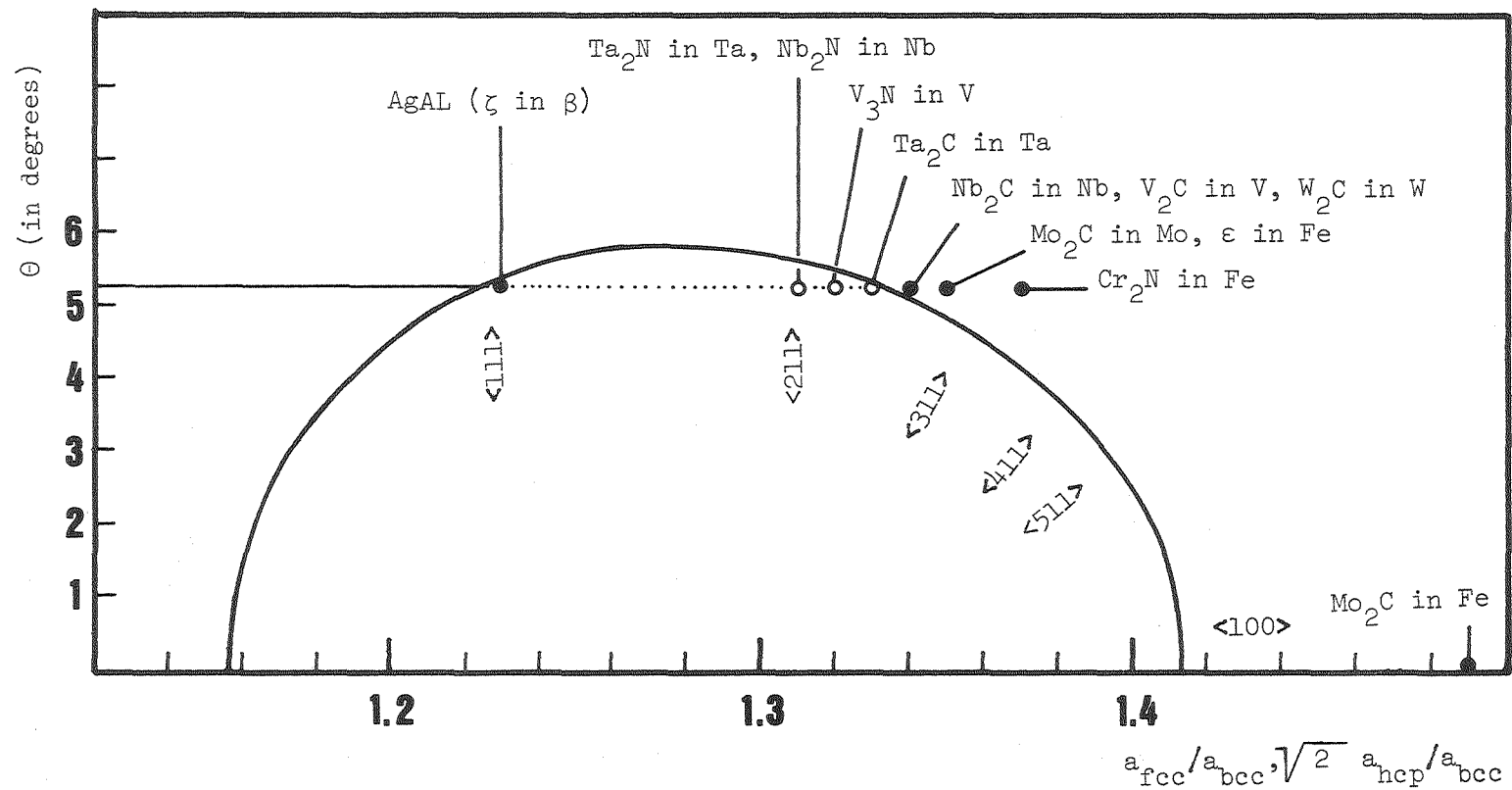
Fig. 5

a   b

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Fig. 6

Fig. 7

XBL 811-7766

Fig. 8

⟨Ī11⟩

⟨Ī1Ī⟩

XBL 8010-12218

a

b

Fig. 9